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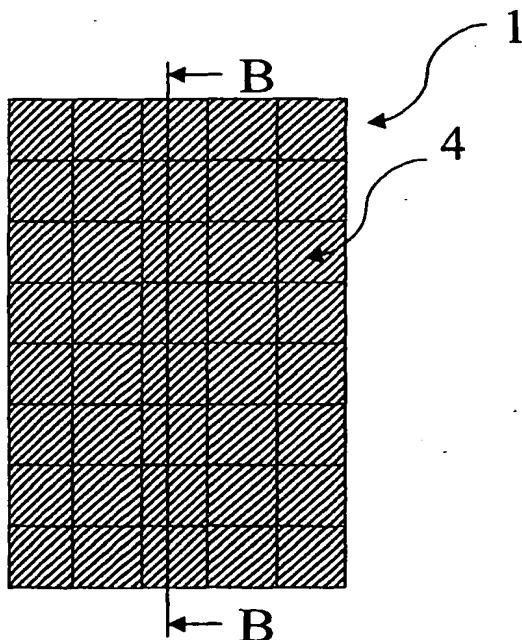
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(54) Title: **FABRIC FOR PROTECTIVE GARMENTS**



(57) Abstract: The present invention relates to a heat, flame, and electric arc resistant fabric (1) for use as single or outer layer of protective garments. The fabric (1) of the invention comprises at least two separate single plies which are assembled together at predefined positions so as to build pockets (4). The fabric (1) of the invention is made of materials independently chosen from the group consisting of aramid fibers and filaments, polybenzimidazol fibers and filaments, polyamidimid fibers and filaments, poly(paraphenylene benzobisaxazole) fibers and filaments, phenol-formaldehyde fibers and filaments, melamine fibers and filaments, natural fibers and filaments, synthetic fibers and filaments, artificial fibers and filaments, glass fibers and filaments, carbon fibers and filaments, metal fibers and filaments, and composites thereof. Due to its peculiar structure, the fabric (1) according to the present invention can have a specific weight which is considerably lower than that of known fabrics having comparable mechanical and thermal properties.

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TITLE OF THE INVENTION

FABRIC FOR PROTECTIVE GARMENTS

BACKGROUND OF THE INVENTION

1. Field of the Invention.

5 The invention relates to a heat, flame and electric arc resistant fabric for use as single or outer layer of protective garments.

2. Description of Related Art.

A garment protecting against heat, flame and electric arc is usually very heavy because the mass and the thickness of the garment itself are normally the main factors conferring protection. The wearer of such a garment, like for example the firefighter, is therefore limited in his movements and undergoes heat stress so that the overall wear comfort strongly decreases. In the last twenty years, attempts have continuously been made to develop new materials in order to improve the wear comfort of such protective garments. For example, lighter but more voluminous insulating materials have been developed for this purpose. These materials confer more lightness to the final protective garment but they might affect the respiratory activities of the wearer due to their cumbersome dimensions. Furthermore, the freedom of movement is not necessarily improved by using these materials.

Garments protecting against heat, flame and electric arc are usually made of one or more layers. The choice of the different materials and of the number of layers constituting the final protective garment depends on the specific application of the garment itself.

25 When designing a new protective garment, care must be taken that all criteria of the relevant national and international norms are fulfilled. As an example, heat and flame resistant garments must be manufactured in accordance with EN-340, EN-531, EN 469 as well as NFPA 1971:2000, NFPA 2112:2001, and NFPA 70E:2000. For instance, a lighter protective garment could be manufactured by simply using lighter materials. However, this is usually associated with a decrease of the mechanical and thermal properties of the protective garment.

U.S. 5,701,606 discloses a firefighter garment having an outer shell and an inner liner functioning as a combined thermal barrier and moisture barrier made of a fire-retardant, closed-cell foam material. The closed-cell foam liner is moisture resistant and provides thermal insulation. The garment disclosed in this prior art document provides good flame resistance but its weight is elevated since it consists of several fabric layers each having a considerable thickness.

U.S. 4,897,886 discloses a firefighter's garment having an outer layer, an intermediate layer and an inner layer. Spacer elements are positioned between two of the layers of the garment thus establishing and maintaining an in-between air gap. The invention disclosed in this prior art document aims to improve the heat resistance of a garment but it is not concerned with its weight and all the problems related thereto which have been mentioned above.

U.S. 4,814,222 discloses aramid fibers which are treated with a swelling agent to improve flame resistance. Such aramid fibers are used for the manufacture of garments which, due to the elevated specific weight of the fibers themselves, are heavy and rigid and, therefore, do not provide an adequate wear comfort.

WO 03/039280, which could be a prior right in Europe according to Articles 54(3) and 54(4) EPC, discloses a multilayer material which can be used as inner liner (thermal barrier) in protective clothing, particularly for fire fighters. WO 03/0392280 is totally silent about the use of such multilayer materials as outer layer or single layer of protective clothing.

The problem at the root of the present invention is therefore to provide a heat, flame and electric arc resistant fabric which, if used as single or outer layer of protective garments, enables to increase wear comfort and to improve the dissipation of vapor and heat produced by the wearer.

BRIEF SUMMARY OF THE INVENTION

Now, it has been surprisingly found that the above mentioned problems can be overcome by a heat, flame, and electric arc resistant

fabric for use as single or outer layer of protective garments, comprising at least two separate single plies each having a warp and a weft system, the at least two separate single plies being assembled together at predefined positions so as to build pockets, the warp and the weft systems of the at least two separate single plies being based on materials independently chosen from the group consisting of aramid fibers and filaments, polybenzimidazol fibers and filaments, polyamidimid fibers and filaments, poly(paraphephenylene benzobisaxazole) fibers and filaments, phenol-formaldehyde fibers and filaments, melamine fibers and filaments, natural fibers and filaments, synthetic fibers and filaments, artificial fibers and filaments, glass fibers and filaments, carbon fibers and filaments, metal fibers and filaments, and composites thereof.

Due to its peculiar structure, the fabric according to the present invention can have a specific weight which is considerably lower than that of known fabrics having comparable mechanical and thermal properties.

Another aspect of the present invention is a garment for protection against heat, flames and electric arc comprising the above fabric as single or outer layer.

The garment according to the present invention strongly improves the wearer's comfort both during normal and critical situations. It is lighter and thinner than conventional garments having similar mechanical and thermal properties and it enables a higher heat and vapor dissipation from the wearer surface to the environment.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a top view of a preferred embodiment according to the present invention.

Fig. 2 is a top view of another preferred embodiment according to the present invention.

Fig. 3a is a cross sectional view of the fabric of Figure 1 before undergoing thermal exposure. This cross sectional view is taken along the line B-B of Figure 1.

Fig 3b is a cross sectional view of the fabric of Figure 1 after undergoing thermal exposure ($T_1 > T_0$). This cross sectional view is taken along the line B-B of Figure 1.

Fig 4a is a cross sectional view of the fabric of Figure 2 before undergoing thermal exposure. This cross sectional view is taken along the line B-B of Figure 2.

Fig 4b is a cross sectional view of the fabric of Figure 2 after undergoing thermal exposure ($T_1 > T_0$) for a period of time up to 3 seconds. This cross sectional view is taken along the line B-B of Figure 2.

Fig 4c is a cross sectional view of the fabric of Figure 2 after undergoing thermal exposure ($T_0 \sim T_1$) for a period of time of more than 3 seconds. This cross sectional view is taken along the line B-B of Figure 2.

Fig 5 is a schematic representation of the weave construction of the fabrics of Examples 1, 2, 4, 5 and 6.

Fig 6 is a schematic representation of the weave construction of the fabric of Example 3.

DETAILED DESCRIPTION OF THE INVENTION

Reference is made to Figures 1 and 3.

Under normal conditions, that is when on both sides of the fabric (1) the temperature equals room temperature T_0 , the plies (2,3) of the fabric (1) are adjacent to each other so that the pockets (4) of the fabric (1) have a substantially flat structure.

In the case of thermal exposure, the ply (2) of the fabric (1), which is exposed to the elevated temperature T_1 (up to 300°C or more) will shrink so that the fabric pockets will swell and form partially air filled chambers which will further isolate the wearer from the environment. An air insulation system is therefore automatically activated when needed during critical situations, thus improving the thermal performance of the fabric without increasing its specific weight.

Aramid fibers and filaments suitable for the manufacture of the fabric of the present invention can have various physical and chemical properties in accordance with the specific application of the fabric itself.

Typically, the aramid fibers and filaments can be selected from the group consisting of poly-m-phenylenisophtalamid (meta-aramid), poly-p-phenylenterephtalamid (para-aramid) and mixtures thereof. Commercially available meta-aramid and para-aramid fibers and filaments are available
5 for example under the trade marks NOMEX® and KEVLAR®, respectively, from E.I. du Pont de Nemours and Company, Wilmington, Delaware, U.S.A.

Natural fibers and filaments which can be used in accordance with the present invention are for example wool, cotton and silk. Artificial fibers
10 and filaments can be selected among viscose and chitosan, while synthetic fibers and filaments can be typically polyester, polyamid and polypropylene. Composites of one or more of such natural, artificial and synthetic fibers and filaments can be also used for the manufacture of the fabric of the present invention.

15 The selection of the different materials depends on the specific application of the fabric according to the present invention.

Typically, each single ply (2,3) of the fabric (1) of the present invention will include large amounts of fibers and filaments of materials having good thermal properties such as aramid, polybenzimidazol,
20 polyamidimid, poly(paraphephenylene benzobisaxazole), phenol-formaldehyde and melamine. However, for certain specific applications, it is appropriate to have one or more plies substantially made with materials like the natural, artificial and synthetic materials mentioned above. For protection against molten metal, for example, the fabric ply which will be
25 directly in contact with the hot metal can advantageously include high amounts (up to 100 wt-%) of wool and viscose in order to create a gliding surface preventing the hot metal particles from sticking thereon.

According to a preferred embodiment of the present invention, the warp and weft systems of the at least two separate single plies are,
30 independently to each other, based on monofilament yarns, multifilament yarns, spun yarns and core spun yarns. By "core spun yarn" is meant in the present invention a mono or multifilament core covered with a fiber

covering. Advantageously, the warp and weft systems of the at least two separate single plies (2,3) are, independently to each other, single yarns, twisted yarns and hybrid yarns. By "hybrid yarns" is meant in the present invention twisted or covered yarns made of filament yarns, spun yarns, 5 core spun yarns and composites thereof.

In a further preferred embodiment of the present invention, the warp and weft systems of the at least two separate single plies (2,3) comprise, independently to each other, single and twisted yarns comprising aramid fibers, aramid monofilaments, aramid multifilaments or composite fibers of 10 aramid and polybenzimidazol.

Advantageously, the warp systems of the fabric of the present invention comprise, independently to each other, single and twisted yarns comprising aramid monofilaments or aramid multifilaments, and the weft systems comprise, independently to each other and in an alternate 15 sequence, single or twisted yarns of aramid monofilaments or single or twisted yarns of aramid multifilaments. Still more advantageously, the weft systems of the fabric of the present invention comprise, independently to each other and in an alternate sequence, at least two different aramid multifilament single and twisted yarns.

20 For many applications, the fabric according to the present invention consists of two separate single plies which can be assembled together, for example, by weaving, knitting, sewing or gluing.

The fabric of the present invention typically comprises aramid fibers chosen from the group consisting of poly-m-phenyleniso-phthalamid, poly- 25 p-phenylenterephthalamid and mixtures thereof. In order to further increase the mechanical properties of the fabric according to the present invention, and if the specific application requires it, the ply which will face the wearer (the internal ply in the garment) will be entirely made of poly-p-phenylenterephthalamid.

30 In accordance with the specific application, as it will be explained below, the two plies can be made of the same material or, alternatively, each ply can be made of a material having a different dimensional thermal

shrinkage. By "dimensional thermal shrinkage" is meant the widthwise and lengthwise contraction of a fiber yarn or fabric on exposure to a heat source.

For applications where the time of exposure to a heat source is up to about 3 seconds, like in the case of electric arc, the two plies of the fabric can be made of the same material. In these situations, the side of the fabric exposed to the elevated temperature T_1 (Fig 3b) will shrink relatively fast so that air filled pockets will be formed rapidly. Due to the short exposure, the temperature T_0 will not have the time to increase up to T_1 so that little shrinkage or no shrinkage at all will be observed at the fabric side facing the wearer. The insulating pockets will therefore maintain their volume during the entire period of exposure.

In order to further increase the insulation effect of the fabric for exposures up to 3 seconds, each separate single ply (2,3) can be made of a material having a different dimensional thermal shrinkage, the ply of the fabric which is exposed to the heat source having the higher dimensional thermal shrinkage. In this way, the difference in shrinkage between the two fabric plies will be still greater during thermal exposure so that still more voluminous air pockets will be formed.

Figures 2 and 4 depict a preferred embodiment for applications where the time of exposure to a heat source is more than 3 seconds. In such situations, for example, in the case of a fire, the fabric of the present invention is preferably made of two separate single plies (2,3) each made of a material having a different dimensional thermal shrinkage, the two separate single plies being woven together in such a way that they cross each other at the predefined positions so that the same side (Figs 2 and 4a, S1 or S2) of two adjacent pockets is alternately made of the two different separate single plies (2,3) according to a chess design. In the first phase of the thermal exposure (up to about 3 seconds, $T_0 < T_1$, Fig 4b), the side (S1) of the fabric exposed to the heat source will shrink relatively fast so that air filled pockets will be formed rapidly. Due to the difference in the dimensional thermal shrinkage of the plies (2,3) and

because of the chess design of the fabric, the adjacent air filled pockets will alternately have two different volumes V_1, V_2 , ($V_1 > V_2$ Fig 4b). In the second phase of the exposure (from 3 seconds up to 8 seconds or more, $T_0 = T_1$, Fig. 4c), the side (S2) will also start to shrink. Due to the chess design of the fabric, and to the difference in the dimensional thermal shrinkage of the two plies (2,3), air filled pockets having a volume V_3 ($V_3 < V_1, V_2$) will be formed on both sides of the fabric according to the shifted configuration depicted in Fig. 4c. Such air filled structure will be maintained during the rest of the time so that an air insulating system will be available during the whole thermal exposure.

Advantageously, the two separate single plies of the fabric according to the present invention are assembled together at predefined positions so as to build closed, adjacent pockets which are preferably square shaped. If compared to e.g. a tubular pockets structure, a square pockets structure provide superior strength and tear resistance in both the warp and weft direction and also provides superior abrasion resistance. Furthermore, such a structure provides more insulation effect because of the relatively small pockets that can respond to local heat inputs in a more efficient way. A square pockets structure confers optimal flexibility to the fabric of the invention and it provides superior visual aesthetics. Such fabric structure is also easier to be formed into a garment since the functionality of the square pockets is not affected by their orientation in the garment itself.

The optimal size of the pockets depends on the specific applications and on the materials used. Generally speaking, the larger the size of the pockets the larger the volume of the air filled pockets which are built during thermal exposure and, therefore, the better the insulation effect. This is, however, true up to a certain limit where the shrinkage of the materials no longer leads to the building of air filled insulation gaps and the fabric remains flat in despite of the thermal exposure. For this reason, each size of the pockets is typically between 5 and 50 mm and, preferably, between 8 and 32 mm.

The specific weight of the fabric according to the present invention is preferably between 100 g/m² and 900 g/m² and, still more preferably, between 170 and 320 g/m².

According to still another preferred embodiment of the present invention, the fabric (1) includes filling yarns which are positioned between the at least two separate single plies (2,3) of the fabric. The filling yarns can be of materials having good thermal properties as those mentioned above, and they aim to increase the thickness of the fabric (1) thus creating further insulating volume during critical conditions such as heat and flames.

A second aspect of the present invention is a garment for protection against heat, flames and electric arc comprising a structure made of at least one layer of the fabric described above.

According to a preferred embodiment of the present invention the garment comprises a structure comprising an internal layer, optionally an intermediate layer made of a breathing waterproof material, and an outer layer made of the above-described fabric of the invention.

According to another preferred embodiment, the fabric of the present invention used for manufacturing the protective garment is made of two separate single plies (2,3), the former being positioned internally and the latter externally in the structure of the garment, the dimensional thermal shrinkage of the internally positioned separate single ply being the same (for example, the same material for both plies) or lower than that of the externally positioned separate single ply. This embodiment is particularly suitable for applications where the garment wearer is exposed to a heat source for periods of time up to 3 seconds, like for example in the case of electric arc.

For expositions to a heat source longer than 3 seconds, a fabric having a chess design, as shown in Fig. 2, can be more appropriate for the reasons mentioned above.

Preferably, the fabric is made of two separate single plies comprising poly-p-phenylenterephthalamid, the internally positioned ply

comprising at least the same amount of poly-p-phenylterephthalamid as the externally positioned ply. For some applications, in order to confer to the garment elevated mechanical properties, the internally positioned ply is entirely made of poly-p-phenylterephthalamid.

5 The internal layer, which faces the body of the wearer, can be an insulating lining made for example of a fabric of two, three or more plies. The purpose of such lining is to have an additional insulating layer further protecting the wearer from the heat.

10 The internal layer can be made of a woven, a knitted or a non-woven fabric. Preferably, the internal layer is made of a fabric comprising non meltable fire resistant materials, such as a fleece or a woven fabric of meta-aramid.

15 The garment according to the present invention can be manufactured in any possible way. It can include an additional, most internal layer made, for example, of cotton or other materials further improving the wearing comfort. The most internal layer directly faces the wearer's skin or the wearer's underwear.

20 The garment according to the present invention can be of any kind including, but not limited to jackets, coats, trousers, gloves, overalls and wraps.

EXAMPLES

The invention will be further described in the following examples.

Example 1

25 A blend of fibers, commercially available from E.I. du Pont de Nemours and Company, Wilmington, Delaware, U.S.A., under the trade name Nomex® N307, having a cut length of 5 cm and consisting of:

93 wt% of pigmented poly-metaphenylene isophthalamide (meta-aramid), 1.4 dtex staple fibers;

30 5 wt% of poly-paraphenylene terephthalamide (para-aramid) fibers; and

2 wt% of carbon core polyamide sheath antistatic fibers

was ring spun into two types of single staple yarns (Y1 and Y2) using a conventional cotton staple processing equipment.

Y1 had a linear density of Nm 60/1 or 167 dtex and a twist of 850 Turns Per Meter (TPM) in Z direction and it was subsequently treated with steam to stabilize its tendency to wrinkle. Y1 was used as weft yarn.

Y2 had a linear density of Nm 70/1 or 143 dtex and a twist of 920 TPM in Z direction. Y2 was subsequently treated with steam to stabilize his tendency to wrinkle. Two Y2 yarns were then plied and twisted together. The resulting plied and twisted yarn (TY2) had a linear density of Nm 70/2 or 286 dtex and a twist of 650 TPM in S direction. TY2 was used as warp yarn...

Y1 and TY2 were woven into a two plies weave fabric having closed square pockets with size 8 mm. The fabric was woven according to the construction depicted in Figure 5. The weave fabric had 42 ends/cm (warp) (21 ends/cm for each ply), 48 weft/cm (weft) (24 ends/cm for each ply) and a specific weight of 200 g/m². The following physical tests were carried out on the thus obtained fabric:

Determination of the breaking strength and elongation according to ISO 5081;

Determination of the tear resistance according to ISO 4674;

Determination of the dimensional change after washing and drying according to ISO 5077;

Combined radiant and convective heat testing according to the TPP method (NFPA 1971:2000, section 6-10, ISO 17492) as a single layer with a heat flux calibrated to 2.0 cal/cm²/s, TPP rating being the energy (cal/cm²) measured to simulate a second-degree burn on the skin of an individual;

Electric arc testing according to ASTM F 1959/F 1959M-99.

The fabric was tested both as single layer (Fabric in Table I) and as the outershell of a multilayer structure (Garment in Table I) which further comprised 1) an intermediate layer of a PTFE membrane laminate on a non-woven fabric made of 85 wt-% Nomex[®] and 15 wt-% Kevlar[®] and

- having a specific weight of 135 g/m^2 (commercially available under the trade name GORE-TEX® Fireblocker N from the company W. L. Gore and Associates, Delaware, U.S.A.), and 2) an internal layer of a meta-aramid thermal barrier having a specific weight of 140 g/m^2 quilted on a 100 wt-%
- 5 Nomex® N 307 fabric having a specific weight of 110 g/m^2 .

The results are given in Table I. The fabric pockets swelled while undergoing the combined radiant and convective heat testing and the electric arc testing.

Table 1

	Warp	Weft
Breaking strength (N)	1390	860
Elongation (%)	38.6	36.4
Tear resistance (N)	72.8	95.5
Dimensional change after washing (%)	-1.0	-2.0
Specific Weight (g/m ²)	200	
TPP (Fabric)		
Time to record pain (s)	4.7	
Second degree burn (s)	7.3	
TPP rating (cal/cm ²)	14.6	
Fabric Failure Factor (10 ⁻² cal/g)	7.3	
TPP (Garment)		
Time to record pain (s)	15.1	
Second degree burn (s)	20.7	
TPP rating (cal/cm ²)	41.5	
Fabric Failure Factor (10 ² cal/g)	7.1	

10

Table 1 shows an excellent performance of the fabric, in particular with regard to the Fabric Failure Factor (FFF), which is defined as follows:

$$\text{FFF} = \text{TPP (cal/cm}^2\text{)} / \text{fabric specific weight (g/m}^2\text{)}.$$

The fabric tested as single layer had an FFF value of 7.3×10^2

15 cal/g while a similar fabric of the same specific weight and the same materials, but woven according to a standard twill construction, had an

FFF value of less than 6.6×10^2 cal/g. This value is considered by the persons skilled in the art to be a sort of technical barrier which conventional single layer fabrics available on the market and having similar weights and made of similar materials have never been able to pass.

The fabric tested as outershell of a multilayer structure had an FFF value of 7.1×10^2 cal/g, while comparable conventional multilayer structures had FFF values ranging between 5.2×10^2 and 6.7×10^2 cal/g.

The electric arc test according to ASTM F1959 generated an ATPV value of about 9.5 cal/cm^2 and an estimated energy to break-open (EBT) measured over a T-shirt of about 12 cal/cm^2 .

Similar fabrics of the same weight and the same materials but woven according to a standard 2/1 twill construction have significantly lower ATPV value, ranging between 4.2 cal/cm^2 and 5.2 cal/cm^2 and similar EBT measured over a T-shirt ranging between 10 cal/cm^2 and 15 cal/cm^2 . To achieve an ATPV value of 9.5 cal/cm^2 , the specific weight of a fabric woven according to a standard 2/1 twill construction must be at least 365 g/m^2 .

This test confirms that the fabric of the invention confers good protection against electric arc despite its relatively low specific weight.

Example 2

Two plies weave fabrics with squared pockets of different sizes were prepared according to Example 1.

For the first ply, Y1 was used as weft and TY2 as warp.

For the second ply, the weft and warp were prepared as follows:

A blend of fibers, commercially available from E. I du Pont de Nemours and Company, Wilmington, Delaware, U.S.A., under the trade name Nomex® N305 having a cut length of 5 cm and consisting of:

75% pigmented poly-metaphenylene isophthalamide (meta-aramid) 1.7 dtex staple fibers;

23% poly-paraphenylene terephthalamide (para-aramid) fibers; and

2 % of carbon core polyamide sheath antistatic fibers

was ring spun into two types of single staple yarns (Y3 and Y4) using a conventional cotton staple processing equipment.

Y3 had a linear density of Nm 60/1 or 167 dtex and a twist of 930 TPM in Z direction, and it was subsequently treated with steam to stabilize its tendency to wrinkle. Y3 was used as weft yarn.

Y4 had a linear density of Nm 70/1 or 143 dtex and a twist of 1005 TPM in Z direction, and it was subsequently treated with steam to stabilize its tendency to wrinkle.

Two Y4 yarns were then plied and twisted together. The resulting plied yarn (TY4) had a linear density of Nm 70/2 or 286 dtex and a twist of 700 TPM in S direction. TY4 was used as warp yarn.

Three weave fabrics having closed square pockets of 8x8, 16x16 and 32x32 mm, respectively were prepared. The three fabrics had 42 ends/cm (warp) (21 ends/cm for each ply), 48 weft/cm (weft) (24 ends/cm for each ply) and a specific weight of 200 g/m². The same physical tests as in Example 1 were carried out on the three fabrics with exception of the electric arc testing according to ASTM F1959.

The fabrics were tested both as single layer (Fabric in Table 2) and as the outershell of the multilayer structure as in Example 1 (Garment in Table 2).

The results are given in Table 2. The pockets of the fabric swelled while undergoing the combined radiant and convective heat testing.

Table 2

Pocket size	8x8 mm		16x16 mm		32x32 mm	
	warp	Weft	warp	weft	warp	weft
Breaking strength (N)	1105	750	1075	700	1065	710
Elongation (%)	10.7	12.1	10.4	11.1	9.7	11.4
Tear resistance (N)	81.0	97.0	78.7	113.2	80.2	115.8
Dimensional change after washing (%)	-0.5	-4.0	-0.0	-4.0	-0.0	-3.5
Specific Weight (g/m ²)	205		204		204	
TPP (Fabric)						
Time to record pain (s)	4.5		4.6		4.9	
Second degree burn (s)	6.8		6.9		7.2	
TPP rating (cal/cm ²)	13.5		13.7		14.5	
Fabric Failure Factor (10 ² cal/g)	6.7		6.9		7.2	
TPP (Garment)						
Time to record pain (s)	14.4		14.8		15.4	
Second degree burn (s)	20.5		20.7		21.4	
TPP rating (cal/cm ²)	40.9		41.3		42.8	
Fabric Failure Factor (10 ² cal/g)	7.0		7.1		7.3	

Table 2 shows an excellent performance of the fabric, in particular with regard to the FFF values which were between 6.7×10^2 and 7.2×10^2 cal/g. A similar fabric of the same specific weight and the same materials but woven according to a standard 2/1 twill construction had an FFF value of 6.6×10^2 cal/g.

The fabrics tested as outershell of a multilayer structure had FFF values between 7.0×10^2 and 7.3×10^2 cal/g, while comparable conventional multilayer structures had FFF values ranging between 5.2×10^2 and 6.7×10^2 cal/g.

Table 2 also shows that the larger the size of the pockets, the better is the performance of the fabric with regard to the TPP test.

Example 3

Two plies weave fabrics with squared pockets of different sizes were prepared using the same materials as in Example 2. The two plies were woven together by alternating them so as to obtain a chess design, as shown in Fig. 2, where the same side of two adjacent pockets is alternately made of the two different separate single plies. The fabric was woven according to the construction depicted in Figure 6.

Three weave fabrics having closed square pockets of 8x8, 16x16 and 32x32 mm, respectively were prepared. The three fabrics had 42 ends/cm (warp) (21 ends/cm for each ply), 48 weft/cm (weft) (24 ends/cm for each ply) and a specific weight of 200 g/m². The same physical tests as in Example 1 were carried out on the three fabrics with exception of the electric arc testing according to ASTM F1959.

The fabrics were tested both as single layer (Fabric in Table 3) and as the outershell of the multilayer structure as in Example 1 (Garment in Table 3).

The results are given in Table 3. The pockets of the fabric swelled while undergoing the combined radiant and convective heat testing.

Table 3

Pocket size	8x8 mm		16x16 mm		32x32 mm	
	Warp	Weft	Warp	Weft	Warp	Weft
Breaking strength (N)	1090	720	1075	700	1070	690
Elongation (%)	10.8	12.1	10.3	11.5	9.6	11.0
Tear resistance (N)	89.6	112.3	107.8	75.4	110.1	78.5
Dimensional change after washing (%)	-1.0	-4.5	-0.5	-4.5	-0.0	-4.5
Specific Weight (g/m ²)	205		203		200	
TPP (Fabric)						
Time to record pain (s)	4.6		4.7		4.9	
Second degree burn (s)	6.9		7.1		7.3	
TPP rating (cal/cm ²)	13.8		14.2		14.6	
Fabric Failure Factor (10 ² cal/g)	6.9		7.1		7.3	
TPP (Garment)						
Time to record pain (s)	14.2		14.8		15.3	
Second degree burn (s)	20.3		20.8		21.6	
TPP rating (cal/cm ²)	40.7		41.6		43.3	
Fabric Failure Factor (10 ² cal/g)	7.0		7.1		7.4	

Table 3 shows an excellent performance of the fabric. The chess design generally confers to the fabrics improved thermal and mechanical

5 properties in case of longer exposure to heat and flames.

In analogy with Example 2, Table 3 also shows that the larger the size of the pockets, the better is the performance of the fabric with regard to the TPP test.

Example 4

10 Two plies weave fabrics with squared pockets were prepared according to Example 1.

For the first ply, Y1 was used as weft and TY2 as warp.

For the second ply, the weft and warp were prepared as follows:
100% Kevlar® stretch broken fibers were ring spun into two types of single staple yarns (Y5 and Y6) using a conventional worsted staple processing equipment.

- 5 Y5 had a linear density of Nm 60/1 or 167 dtex and a twist of 575 TPM in Z direction, and it was subsequently treated with steam to stabilize its tendency to wrinkle. Y5 was used as weft yarn.

- Y6 had a linear density of Nm 70/1 or 143 dtex and a twist of 620 TPM in Z direction, and it was subsequently treated with steam to stabilize
10 its tendency to wrinkle.

Two Y6 yarns were then plied and twisted together. The resulting plied yarn (TY6) had a linear density of Nm 70/2 or 286 dtex and a twist of 600 TPM in S direction. TY6 was used as warp yarn.

- A fabric weave having closed square pockets of 8x8 was prepared.
15 This fabric had 42 ends/cm (warp) (21 ends/cm for each ply), 48 weft/cm (weft) (24 ends/cm for each ply) and a specific weight of 200 g/m². The same physical tests as in Example 1 were carried out on this fabric with exception of the electric arc testing according to ASTM F1959.

- The fabric was tested both as single layer (Fabric in Table 4a) and
20 as the outershell of the multilayer structure as in Example 1 (Garment in Table 4a).

The results are given in Table 4a. The pockets of the fabric swelled while undergoing the combined radiant and convective heat testing.

Table 4a

	warp	weft
Breaking strength (N)	3045	2080
Elongation (%)	10.5	8.7
Tear resistance (N)	208	294
Dimensional change after washing (%)	-1.5	-2.5
Specific Weight (g/m ²)	208	
TPP (Fabric)		
Time to record pain (s)	4.6	
Second degree burn (s)	7.0	
TPP rating (cal/cm ²)	14.1	
Fabric Failure Factor (10 ² cal/g)	7.0	
TPP (Garment)		
Time to record pain (s)	16.7	
Second degree burn (s)	23.4	
TPP rating (cal/cm ²)	46.9	
Fabric Failure Factor (10 ² cal/g)	8.0	

Table 4a shows an excellent performance of the fabric in particular as an
 5 outershell in a multilayered construction with the highest FFF value at 8.0
 $\times 10^2$ cal/g. The physical performance of the fabric with regard to breaking
 strength and tear resistance is also excellent. A fabric with the same
 components and specific weight, but woven according to a standard
 monolayer construction, would show approximately half of this
 performance.

10 The fabric was tested as single layer in accordance with the TATE
 (Tensile After Thermal Exposure) method:

The TATE method is based on the determination of breaking
 strength and elongation (Strip method) according to the standard ISO
 5081 after TPP exposures of 2 s and 4 s with a heat flux calibrated to 2.0
 15 cal/cm²/sec.

The test conditions were :

Testing machine: constant rate of traverse (CRT) with a
load cell of 2000N

5 Gauge length: 200 ± 1 mm
Sample width: 50 ± 0.5 mm
Speed of traverse: 100 mm/min.

The results are summarized in Table 4b.

10

Table 4b

		0s	2s	4s
Breaking strength	N	2780	2395	895
Elongation at break	%	9.4	10.1	7.3

Conventional fabrics currently used in Europe as outershell of firefighter
turn out coats have a weight-normalized TATE value after 4 seconds (the
TATE value divided by the fabric specific weight) ranging between 1.8 N g^{-1}
15 cm^2 and $3.3 \text{ N g}^{-1} \text{cm}^2$, while the fabric of this Example has a value of
about $4.5 \text{ N g}^{-1} \text{cm}^2$. This clearly shows that this fabric is particularly
suitable as outershell of protective garments for fire fighters.

Example 5

20 Two plies weave fabrics with squared pockets were prepared
according to Example 1.

For the first ply, the weft and warp were prepared as follows: A
blend of 50% Kevlar® and 50% Nomex® long staple fibers were ring spun
into two types of single staple yarns (Y7 and Y8) using a conventional
worsted staple processing equipment.

25 Y7 had a linear density of Nm 60/1 or 167 dtex and a twist of 575
TPM in Z direction, and it was subsequently treated with steam to stabilize
its tendency to wrinkle. Y7 was used as weft yarn.

Y8 had a linear density of Nm 70/1 or 143 dtex and a twist of 620 TPM in Z direction, and it was subsequently treated with steam to stabilize its tendency to wrinkle.

Two Y8 yarns were then plied and twisted together. The resulting
5 plied yarn (TY8) had a linear density of Nm 70/2 or 286 dtex and a twist of 600 TPM in S direction. TY8 was used as warp yarn.

For the second ply, Y5 was used as weft and TY6 as warp.

A fabric weave having closed square pockets of 8x8 was prepared. This fabric had 42 ends/cm (warp) (21 ends/cm for each ply), 48 weft/cm
10 (weft) (24 ends/cm for each ply), and a specific weight of 200 g/m². The same physical tests as in Example 1 were carried out on this fabric. The fabric was tested both as single layer (Fabric in Table 5a) and as the outershell of the multilayer structure as in Example 1 (Garment in Table 5a).

15 The results are given in Table 5a. The pockets of the fabric swelled while undergoing the combined radiant and convective heat testing and the electric arc testing.

Table 5a

	warp	weft
Breaking strength (N)	3575	2940
Elongation (%)	10.9	6.4
Tear resistance (N)	249	343
Dimensional change after washing (%)	-1.5	-1.5
Specific Weight (g/m ²)	210	
TPP Single layer		
Time to record pain (s)	4.3	
Second degree burn (s)	6.7	
TPP rating (cal/cm ²)	13.5	
Fabric Failure Factor (10 ² cal/g)	6.7	
TPP Garment		
Time to record pain (s)	15.5	
Second degree burn (s)	21.4	
TPP rating (cal/cm ²)	42.9	
Fabric Failure Factor (10 ² cal/g)	7.3	

Table 5a shows an excellent thermal performance of the fabric in particular as an outershell in a multilayer construction with an FFF of 7.3 x 10² cal/g. Fabric physical properties like breaking strength and tear resistance are also excellent.

The electric arc test according to ASTM F1959 generated an EBT measured over a T-shirt of about 22 cal/cm², thus confirming that this fabric is excellent for protection against electric arc.

Similar fabrics of the same specific weight and the same materials but woven according to a standard 2/1 twill construction have significant lower EBT values, ranging between 10 cal/cm² and 15 cal/cm².

The fabric was tested as single layer in accordance with the TATE method as described in Example 4.

The results are summarized in Table 5b.

Table 5b

		0s	2s	4s
Breaking strength	N	3600	3360	890
Elongation at break	%	10.7	10.3	7.4

Conventional fabrics currently used in Europe as outershell of firefighter turn out coats have a weight-normalized TATE value after 4 seconds (the TATE value divided by the fabric specific weight) ranging between $1.8 \text{ N g}^{-1} \text{ cm}^2$ and $3.3 \text{ N g}^{-1} \text{ cm}^2$, while the fabric of this Example has a value of about $4.5 \text{ N g}^{-1} \text{ cm}^2$. This clearly shows that this fabric is particularly suitable as outershell of protective garments for fire fighters.

Example 6

A two plies weave fabric with squared pockets was prepared according to Example 1.

A Nomex[®] T 430 filament yarn of 220 dtex (Y9) was used as weft and warp for the first ply.

The weft and warp of the second ply were prepared as follows.

A blend of fibers, commercially available from E.I. du Pont de Nemours and Company, Wilmington, Delaware, U.S.A., under the trade name Nomex[®] E502, having a cut length of 5 cm and consisting of:

93 wt% of semi-crystallized ecru poly-metaphenylene isophthalamide (meta-aramid), 1.4 dtex staple fibers;
5 wt% of poly-paraphenylene terephthalamide (para-aramid) fibers;
and

2 wt-% of carbon core polyamide sheath antistatic fibers was ring spun into two types of single staple yarns (Y10 and Y11) using a conventional cotton staple processing equipment.

Y10 had a linear density of Nm 60/1 or 167 dtex and a twist of 850 Turns Per Meter (TPM) in Z direction, and it was subsequently treated with steam to stabilize its tendency to wrinkle. Y10 was used as weft yarn.

Y11 had a linear density of Nm 70/1 or 143 dtex and a twist of 920 TPM in Z direction. Y11 was subsequently treated with steam to stabilize

his tendency to wrinkle. Two Y11 yarns were then plied and twisted together. The resulting plied and twisted yarn (TY11) had a linear density of Nm 70/2 or 286 dtex, and a twist of 650 TPM in S direction. TY11 was used as warp yarn.

- 5 Y10 and TY11 were woven into a two plies weave fabric having closed square pockets with size 32 mm. The weave fabric had 42 ends/cm (warp) (21 ends/cm for each ply), 48 weft/cm (weft) (24 ends/cm for each ply) and a specific weight of 210 g/m². The same physical tests as in Example 1 were carried out on the fabric with exception of the
- 10 electric arc testing according to ASTM F1959.

The results are given in Table 6. The fabric pockets swelled while undergoing the combined radiant and convective heat testing.

Table 6

	Warp	weft
Breaking strength (N)	1350	1170
Elongation (%)	31.5	27.4
Tear resistance (N)	120.2	118.2
Dimensional change		
After washing (%)	-1.0	-3.0
Specific Weight (g/m ²)	210	
TPP Single layer		
Time to record pain (s)	4.4	
Second degree burn (s)	7.4	
TPP rating (cal/cm ²)	14.9	
Fabric Failure Factor (10 ² cal/g)	7.1	
TPP Garment		
Time to record pain (s)	16.3	
Second degree burn (s)	22.9	
TPP rating (cal/cm ²)	45.7	
Fabric Failure Factor (10 ² cal/g)	7.7	

Table 6 shows an excellent thermal performance of the fabric, both as single layer and as outershell in a multilayer structure. The physical properties of the fabric such as the breaking strength and the tear resistance are also excellent. This fabric is particularly suitable for the manufacture of racing suits due to its visual aesthetic (silky appearance) and its excellent protection versus lightness ratio.

The same performance is currently achieved with conventional single layer fabrics having a total specific weight of more than 400g/m².

CLAIMS

What is claimed is:

1. Heat, flame, and electric arc resistant fabric (1) for use as single or outer layer of protective garments, characterized in that it comprises at least two separate single plies (2,3) each comprising a warp and a weft system, the at least two separate single plies (2,3) being assembled together at predefined positions so as to build pockets having a side (S1) and a side (S2), the warp and the weft systems of the at least two separate single plies (2,3) being based on materials independently chosen from the group consisting of aramid fibers and filaments, polybenzimidazol fibers and filaments, polyamidimid fibers and filaments, poly(paraphenylene benzobisaxazole) fibers and filaments, phenol-formaldehyde fibers and filaments, melamine fibers and filaments, natural fibers and filaments, synthetic fibers and filaments, artificial fibers and filaments, glass fibers and filaments, carbon fibers and filaments, metal fibers and filaments, and composites thereof.
2. The fabric (1) according to claim 1, wherein the warp and weft systems of the at least two separate single plies (2,3) are, independently to each other, based on monofilament yarns, multifilament yarns, spun yarns and core spun yarns.
3. The fabric (1) according to claim 1 or 2, wherein the warp and weft systems of the at least two separate single plies (2,3) are, independently to each other, single yarns, twisted yarns and hybrid yarns.
4. The fabric (1) according to claim 3, wherein the warp and weft systems of the at least two single plies (2,3) comprise, independently to each other, single and twisted yarns comprising aramid fibers, aramid monofilaments, aramid multifilaments or composite fibers of aramid and polybenzimidazol.
5. The fabric (1) according to claim 3 or 4, wherein the warp systems of the at least two single plies (2,3) comprise, independently to each other, single and twisted yarns comprising aramid monofilaments or aramid multifilaments, and the weft systems comprise, independently to each

other and in an alternate sequence, single or twisted yarns of aramid monofilaments or single or twisted yarns of aramid multifilaments.

6. The fabric (1) according to claim 5, wherein the weft systems of the at least two single plies (2,3) comprise, independently to each other and in an alternate sequence, at least two different single and twisted yarns of aramid filaments.

7. The fabric (1) according to any preceding claim consisting of two separate single plies (2,3).

8. The fabric (1) according to claim 7, wherein the two separate single plies (2,3) comprise aramid fibers chosen from the group consisting of poly-m-phenylenisophthalamid, poly-p-phenyleneterephthalamid and mixtures thereof.

9. The fabric (1) according to claim 8, wherein one of the two single plies is entirely made of poly-p-phenyleneterephthalamid.

10. The fabric (1) according to any claim 7 to 9, wherein the two separate single plies (2,3) are made of the same material.

11. The fabric (1) according to any claim 7 to 9, wherein each separate single ply (2,3) is made of a material having a different dimensional thermal shrinkage.

12. The fabric (1) according to any claim 7 to 11, wherein the two separate single plies (2,3) are woven together in such a way that they cross each other at the predefined positions so that the same side (S1 or S2) of two adjacent pockets is alternately made of the two different separate single plies (2,3).

13. The fabric (1) according to any claim 7 to 12, wherein the two separate single plies (2,3) are assembled together at predefined positions so as to build closed, adjacent pockets.

14. The fabric (1) according to claim 13, wherein the closed, adjacent pockets are square shaped.

15. The fabric (1) according to any preceding claim, wherein each side of the pockets is between 5 and 50 mm.

16. The fabric (1) according to claim 15, wherein each side of the pockets is between 8 and 32 mm.
17. The fabric (1) according to any preceding claim, having a specific weight between 100 g/m² and 900 g/m².
- 5 18. The fabric (1) according to claim 17, having a specific weight between 170 and 320 g/m².
19. The fabric (1) according to any preceding claim, wherein filling yarns are positioned between the at least two separate single plies (2,3).
20. Garment for protection against heat, flames and electric arc
- 10 comprising a structure made of at least one layer of a fabric (1) according to any claim 1 to 19.
21. The garment according to claim 20, comprising an internal layer, optionally an intermediate layer made of a breathing waterproof material, and an outer layer made of the fabric according to any claim 1 to 19.
- 15 22. The garment according to claim 20 or 21, wherein the fabric (1) is made of two separate single plies (2,3), the former being positioned internally and the latter externally in the structure of the garment, the dimensional thermal shrinkage of the internally positioned separate single ply being lower than that of the externally positioned separate single ply.
- 20 23. The garment according to claim 22 wherein the two separate single plies comprise poly-p-phenylterephthalamid, the internally positioned ply comprising at least the same amount of poly-p-phenylterephthalamid as the externally positioned ply.
24. The garment according to claim 23 wherein the internally positioned
- 25 ply is entirely made of poly-p-phenylterephthalamid.

INTERNATIONAL SEARCH REPORT

Inte. plication No
PC 03/03701

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A41D31/00 D03D15/12 D03D11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A41D D03D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/64985 A (MARCANADA INC ; BARBEAU CLAUDE (CA); COCHRAN ROSS (CA)) 7 September 2001 (2001-09-07) page 4, line 4 - page 6, last paragraph page 7, last paragraph - page 8, line 25; claims 1-14,18-28,31-34; figures 1,2	1-3,7-9, 20,22,24
X	US 2 884 018 A (DELCELLIER HENRI A ET AL) 28 April 1959 (1959-04-28) column 1, line 15 - column 5, line 30; claims 1,2,4,5; figures 1-4d ----- -/--	1,3,12, 13,19,20

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/57738 A (BEKAERT SA NV ; GUCHT ANN V D (BE); HEIRBAUT GUIDO (BE); STEENLANDT WI) 5 October 2000 (2000-10-05) page 6, line 14 - page 9, line 12 page 11, paragraph 1 - paragraph 3 page 13, line 25 - last paragraph page 18, paragraph 2 - page 19, paragraph 3; claims 1,2,4,7-9,23,24; figures 2,6,7,12	1-3,7, 20,21
A	WO 00/66823 A (A W HAINSWORTH & SONS LTD ; HAINSWORTH THOMAS (GB); WALKER DEREK (GB)) 9 November 2000 (2000-11-09) page 2, paragraph 2 - page 6, paragraph 1; claims 1,3-6,8	1,2,4,9, 20,22,24
A,P	WO 03/039280 A (KERMEL ; THIRIOT LAURENT (FR)) 15 May 2003 (2003-05-15) cited in the application page 5, last paragraph - page 9, last paragraph; claims 1-3,7; figure 2.7	1,7,13, 20,22

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 03/03701

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0164985	A	07-09-2001	AU WO 3905001 A 0164985 A2	12-09-2001 07-09-2001
US 2884018	A	28-04-1959	NONE	
WO 0057738	A	05-10-2000	AU WO EP JP 3806700 A 0057738 A2 1164881 A2 2002540312 T	16-10-2000 05-10-2000 02-01-2002 26-11-2002
WO 0066823	A	09-11-2000	AU EP WO US 4418500 A 1173635 A1 0066823 A1 6699802 B1	17-11-2000 23-01-2002 09-11-2000 02-03-2004
WO 03039280	A	15-05-2003	FR WO 2831771 A1 03039280 A1	09-05-2003 15-05-2003

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